

COMPUTATIONAL RECONNAISSANCE OF THE CATALYTIC
PROPERTIES OF MANGANESE NON-PINCER COMPLEXES

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ABSTRACT

The best available catalysts for the reduction of carbonyl groups in ketones are currently based on rare metals such as platinum, osmium or ruthenium. The development of alternative catalysts made from more abundant metal such as manganese offers chances to increase sustainability and cost efficiency. Analysing and predicting chemical and physical properties with a computational would streamline the development process by allowing early elimination of options and by proposing new structures with a high chance of success. Density-functional theory (DFT) can predict structures and ligand properties at a high level.

In this investigation, around 40 ligands were defined based on previously researched manganese compounds with known catalytic properties or previously investigated ruthenium complexes. Properties such as hydricity, CO frequencies and bond lengths were calculated and linked to known catalytic activity from the literature.

No hard correlations between the investigated properties and reported catalytic activities have been found. Some links however do appear to exist such as a connection between high calculated hydricities and a higher reported catalytic activity.

CONTENTS

| | | |
|-------|--|----|
| 1 | INTRODUCTION | 1 |
| 1.1 | Computational Details | 2 |
| 1.2 | Previous Work | 3 |
| 1.2.1 | Nickel | 4 |
| 1.2.2 | Ruthenium | 5 |
| 1.2.3 | Rhodium | 6 |
| 1.2.4 | Iridium | 6 |
| 1.2.5 | Manganese | 7 |
| 2 | MATERIALS & METHOD | 9 |
| 2.1 | Ligands used | 9 |
| 2.2 | Models made | 13 |
| 2.3 | Parameters evaluated | 13 |
| 2.4 | MolSimplify | 14 |
| 3 | RESULTS & DISCUSSION | 19 |
| 3.1 | The CO ligands | 19 |
| 3.2 | Other parameters | 21 |
| 3.3 | Comparison with known catalytic activity | 23 |
| 4 | FUTURE WORK | 25 |
| 4.1 | Finding a correlation for the TEP in manganese bidentate complexes | 25 |
| 4.2 | Alternatives for the TEP | 25 |
| 4.3 | MolSimplify | 26 |
| 5 | SUPPORTING INFORMATION | 27 |

LIST OF FIGURES

| | | |
|-------------|---|----|
| Figure 2.1 | Ligands based on [Pidko, 2018] | 9 |
| Figure 2.2 | Ligands based on [Pidko, 2019a] | 9 |
| Figure 2.3 | Ligands based on [Sortais, 2017] | 10 |
| Figure 2.4 | Ligands based on [Sortais, 2018] | 10 |
| Figure 2.5 | Ligands based on [Sortais, 2019] | 11 |
| Figure 2.6 | Ligands based on [Pidko, 2019b] | 11 |
| Figure 2.7 | Ligands based on [Pathak, 2019] | 12 |
| Figure 2.8 | Ligands based on [Leitner, 2018] | 12 |
| Figure 2.9 | All models per ligand | 13 |
| Figure 2.10 | The molSimplify GUI | 14 |
| Figure 2.11 | Entering the desired ligands in the GUI | 16 |
| Figure 2.12 | The structure generated | 16 |
| Figure 2.13 | The 'Draw ligands' popup window | 17 |
| Figure 2.14 | Generating complex NN01 | 17 |
| Figure 2.15 | Complex NN12 generated by molSimplify | 18 |
| Figure 2.16 | Ethylenediamine, the database version on the left | 18 |
| Figure 2.17 | Window for inserting ligands to the database | 18 |
| Figure 3.1 | A1 frequency vs CO bond length | 19 |
| Figure 3.2 | A1 frequency vs CO1 enthalpy | 20 |
| Figure 3.3 | CO bond length vs CO1 enthalpy | 20 |
| Figure 3.4 | Sum bond length vs BDE ligand (All) | 21 |
| Figure 3.5 | Sum bond length vs BDE ligand (NN) | 21 |
| Figure 3.6 | A1 frequency vs hydricity | 22 |
| Figure 3.7 | A1 frequency vs acidity | 22 |
| Figure 3.8 | Ligands 21, 33 and 34 | 23 |
| Figure 3.9 | Scheme by Sortais | 24 |
| Figure 3.10 | Conversion rate vs A1 frequency | 24 |
| Figure 3.11 | Conversion rate vs hydricity | 24 |
| Figure 3.12 | Conversion rate vs acidity | 24 |

The reduction of carbonyl groups and plays an important role in various organic synthesis pathways. It is relevant in a wide range of areas, both biological and industrial. The reduction of ketones and aldehydes to their corresponding alcohols are important for the production of agrochemical products, perfumes, pharmaceuticals and many other products. [Lei, 2019]

One particular area of interest is the reduction of CO₂ molecules. [DuBois, 2000] Developing efficient catalysts for CO reduction could in theory lead to an efficient method to fixate CO₂ molecules from the atmosphere or from places of emission into more chemically useful compounds. [Mizuno, 2012] This could contribute greatly to reducing our collective reliance on crude oil as a raw material and energy source and possibly help slow or revert the threat of climate change.

This makes catalytic reduction a highly investigated subject. The most common inorganic catalysts for these reactions are transition metal hydride complexes. [Kubiak, 2018] Metal complexes consisting of various metal such as Pt, Ir, Ni, Mn and many other have been described in connection to these reactions. [Kubiak, 2018]. Some of the best catalytic results have been obtained by using the noble metals such as Pt, Rh or Ir. [Zsigmond, 2015] Those complexes do not, however, present a sustainable solution of the desired catalytic needs. High prices and low availability of the these metals make them unattractive for widespread use.

Promising alternatives to Pt and Ir based complexes, which are based on cheaper materials like Mn, are more readily available and sustainable. [Sortais, 2018] Traditionally these metal-complex catalysts have often used phosphines ligands to influence the availability of electrons for catalytic interactions. The use of phosphines presents a range of practical problems due to its toxicity and combustibility. It is therefore desirable to find alternative ligands for these complexes. The desired eventual outcome is a catalyst based on sustainable earth-abundant metal-complexes. [Pidko, 2019a]

Previous work suggests a wide range of different kinds of ligands that could be suitable for the purpose. The experimental evaluation of these different ligands is a time consuming and tedious process. Not all ligands are commercially available and have to be synthesised. The obtained compounds then have to be tested for complex formation and finally their catalytic activities have to be assessed. A lot of these complexes show some catalytic activity, but in the vast majority this activity is minor or even completely absent. A lot of time and resources could be saved, if a non-experimental way of assessing the various complexes is used for a first evaluation of all available options. Those with very low chances of success should then be eliminated and focus should be placed on the compounds with higher chances of success.

Catalytic activity is a complex property, which is not easily accessed. It is highly variable and depends on factors such as substrate, solvent, reaction time, molarity of various compounds involved and many more. Almost all comparative studies make significant concessions to this by first determining optimal conditions for a reference catalyst and substrate and then using these conditions for the entire range of catalysts and substrates. [Pidko, 2017] If anything, this shows the extreme challenges faced in the field of catalysis. A theoretical computational tool might hopefully provide a baseline assessment of different complexes and then limit the scope of the experimental work.

Developing such a computational tool is not a straightforward task. All the previously mentioned problems about catalytic activity are still present in a computational environment. It would be folly to claim such a tool could ever replace experimental work. What could be done, is looking for patterns in the computational data of compounds with known catalytic activities. Ideally, a correlation exists between the catalytic activity and certain properties of the complex that can be calculated. A second best would be the ability to properly assess certain features via computations that increase the likelihood of certain behaviour in experimental studies.

There is quite some work done on this topic, and the most commonly used method involves Density Functional Theory (DFT) calculations. This is a computational quantum mechanical modelling method used to investigate the electronic structure of complex systems, such as metal-ligand complexes. This can be used to determine the spatial structure of a metal complex, calculated spectroscopic properties and derive various thermodynamic values. [Gusev, 2009b]

1.1 COMPUTATIONAL DETAILS

In this section we will define the computational details of various parameters that we encounter during the investigation into computational tools for catalytic reductions of CO groups. The exact meaning and relevance of these parameters will be discussed in the “Previous Work” section.

The hydricity is defined as the free energy associated with the $\text{ML}_n\text{H}^{n-} \rightleftharpoons \text{ML}_n^{(n+1)-} + \text{H}^-$ equilibrium. [Kubiak, 2018] This can be calculated if the Gibbs free energies of the complex (ML_nH^{n-}) and its derivative ($\text{ML}_n^{(n+1)-}$) as well as the hydride anion are known, and these Gibbs free energies can be found using DFT calculations. [DuBois, 2016]

Just like hydricity the pK_A can be evaluated by DFT calculations using the free energy associated with the $\text{ML}_n-\text{H} \rightleftharpoons \text{ML}_n^- + \text{H}^+$ equilibrium. [Kubiak, 2018]

Bond Dissociation Enthalpy and Ligand Exchange Energies are calculated in more or less the same way as hydricity or acidity. The relevant equilibrium needs to be found, the species involved need to be modelled and DFT can be used to find the free Gibbs energies or enthalpies related to all those species. Thus the desired energies or enthalpies can be calculated.

Bond Dissociation Enthalpies can both be evaluated for the situations wherein the ligand is completely detached from the rest of the complex and partial separations. In both cases the procedure remains to describe and model the relevant equilibrium (which might involve a shift from a 6 to 5 coordinate metal) and determine the free Gibbs energies or enthalpies.

The Tolman’s Electronic Parameter (TEP) is defined as the A_1 frequency of a carbonyl group in a metal-ligand complex. [Tolman, 1977] The A_1 stretching vibration in Tolman’s original work is the frequency of the symmetric simultaneous stretch of the three CO bonds, where they expand and contract in unison. Complexes such as Tolman’s with multiple CO groups will also have asymmetric stretches. In an asymmetric stretch one of the CO bonds is contracting, while the others are expanding. [Libretexts, 2020]

The A_1 band is easily measured by IR spectroscopy because it is sharp and often in a part of the spectrum that is otherwise empty. The used phosphorus ligands could be ranked in an electronic series based on the CO stretching frequencies. All of these frequencies can also be evaluated and visualised using DFT calculations.

Determining frequencies of other groups, such as the C=C group by DFT, involves exactly the same process as finding the A_1 frequency of a carbonyl group. Once the frequencies in a complex have been calculated, all of them can easily be accessed and used for comparison or correlation. [Gusev, 2016]

Bond lengths are also easily obtainable by DFT calculations. It requires only the operation of finding an optimized atomic structure, where the xyz-coordinates of all the atoms can be used to generate a distance matrix in which all internal distances between atoms are tabulated. The majority of these distances are of course meaningless and inconsequential, but any distance that could be of interest can be retrieved from this DFT result. When the distance between the central metal and the ligand as a whole is required, the parameter used is the distance between the metal and the connecting atom within the ligand. This means that one ligand can have multiple distances due to its bidentate or pincer nature. [Gusev, 2016]

The buried volume ($\%V_{Bur}$) of ligands is used as a steric descriptor. It quantifies the percentage of the volume of a sphere occupied by a ligand. [Nolan, 2010] This can be calculated using steric maps of various sections of the co-ordination sphere with a 3.5 Å radius. The method for this was developed by Cavallo c.s. [Cavallo, 2010]

1.2 PREVIOUS WORK

Structure-activity [Pidko, 2018], structure-property [Kühl, 2005] and activity-property [Kubiak, 2018] relationships have been widely studied in the past. Before presenting our own study, we will first discuss some of the computational work that has been done on Ni complexes and various kinds of ligands. After that we will expand into other kinds of metal i.e ruthenium, rhodium, iridium and manganese. All of these metals have extensive amounts of experimental work done in catalytic reduction. We will focus on computational work and establishing links between catalytic activity and other parameters, which can be evaluated by calculations.

Any computational study should first ensure that the values that it calculates are good representations of the actual values of the parameters that are investigated. This means the validity of calculated frequencies and energies has to be established. There is one broad study done on a wide variety of metals that is important in establishing validity. [Kühl, 2005]

The most common complexes that were investigated are Ni complexes with phosphine ligands. This is based on the work of Tolman and his coworkers from over 40 years ago. [Tolman, 1977] In this work Tolman used experimental methods to determine an electronic and a steric parameter that described the electronic donor strength of a ligand. $\text{Ni}(\text{CO})_3\text{L}$ was used as a reference complex with several tertiary phosphine ligands. The electronic parameter that his work described is nowadays known as Tolman's Electronic Parameter (TEP).

TEP is evaluated in complexes of all kinds of metal because a systematic analysis of ligands with various kinds of metals established the applicability of the TEP on other metals than Ni. [Kühl, 2005] In his study Kühl and his colleagues determined experimentally A_1 stretching frequencies for carbonyl groups for complexes with 18 different ligands and carbonyl groups. The Ni complexes yielded the TEP for the ligands and were used as a benchmark to compare the frequencies of 13 different metals. This shows that the values of the frequencies depend on which metal is used. More importantly however it showed that the general order of the values is (most of the time) preserved. The ligands with the highest values in the Ni complex, also have the highest value in a Fe, V or Mn complex. This paper also shows that linear correlations exist between the A_1 stretching frequencies of the same ligands in complexes of different metals. These correlations make it possible to correlate a frequency found for a ligand value to the original TEP scale which was based on a $\text{Ni}(\text{CO})_3\text{L}$. This means that TEP can be used to a wide range of other metals, such as manganese, iron, vanadium, rhenium and several others. [Kühl, 2005] This means that TEP can be seen as primarily a descriptor of the ligand, independent of the type of metal to which the ligand is attached. Determining TEP values for a ligand is possible in complexes containing other metals if the correlation between that metal's A_1 frequencies and the TEP values are known.

Other work has raised doubts about the usefulness of the TEP. In a 2017 study Cremer and his colleagues propose replacing the TEP, which evaluates properties of a ligand, via a separate carbonyl group with a metal–ligand electronic parameter (MLEP) that is based on the local stretching force constant of the M–L bond. [Cremer, 2017] This MLEP evaluates individual bonds instead of the ligand as a whole, and does so based on direct information about the bond instead of via a separate carbonyl group. This means that it enable us to identifies weak M–L bonds with promising catalytic activity.

1.2.1 Nickel

The validity of DFT calculations with respect to calculating A_1 stretching frequencies was shown by Perrin and colleagues. [Perrin, 2001] Their research on Ni complexes compared computationally derived ligand electronic parameter (CEP) with experimental TEPs. The study involved 68 different ligands. These ligands included phosphines but also other types such as a wide range of carbenes and various chelating ligands. The values yielded a correlation between TEP and CEP of $TEP = 0.9572CEP + 4.081$ with a 0.996 correlation coefficient. This shows that calculated A_1 frequencies are an efficient and reliable way to obtain the TEP of any ligand without experimental limitations.

A study by Rousseau and his colleagues [Rousseau, 2011] established that DFT can predict with high confidence all relevant energetics for H_2 oxidation and production for Ni(diphosphine)₂ complexes, including hydricities and acidities. Rousseau c.s. concluded that their approach can be extended to other catalysts and other metals, such as platinum, laying the groundwork for our research into manganese based complexes using non-phosphine ligands based on DFT.

It is important to examine the hydride donor abilities of the complex because the rate determining step of the catalytic process depends on it. Analysing the mechanisms of the reactions we tried to catalyse, we found that the reduction of CO_2 or carbonyl bonds always requires the cleavage of at least one C–O bond and the formation of one or more C–H bonds. Important, often rate determining, steps in the catalytic pathways of these reactions depend on the hydride donor ability of the complexes, which is also known as their (thermodynamic) hydricity. [DuBois, 2000] Higher hydricity therefore means easier loss of the hydride and therefore a stronger contribution to catalysis.

We evaluated the acidity of a complex because it can also be related to the catalytic reduction of CO bonds. The availability of another hydrogen atom in close proximity to the hydride ligand can also play a role in catalytic reduction. [Pathak, 2019; Gusev, 2009b; Pidko, 2018] These hydrogen atoms are often part of an amine or sometimes an alcohol group. Amine groups are more likely because a lot of ligands use nitrogen atoms to bind to the metal atom. When these hydrogen atoms are released, they do so in the form of H^+ . Evaluating the strength of this interaction means evaluating the acid strength of the group, which is customarily expressed by the pK_A . Higher acidity means easier lose of the hydrogen atom and therefore a stronger contribution to catalysis.

Bond lengths in the carbonyl groups with the catalytic complex are relevant, because a correlation between the donor properties and the length of the CO bond has been observed by Gusev investigating heterocyclic carbenes in $Ni(CO)_3(NHC)$ complexes. [Gusev, 2009b] A higher frequency (around 2030–2040 cm^{-1}) correlates with higher (between 1.144 to 1.146 Å) C–O distances. This means that both the frequency and the bond length of the carbonyl group can both be linked to information about the desired properties. Many studies still use complexes containing three carbonyl groups.

The bond length in the carbonyl is also valuable, because Gusev's work on $Ni(CO)_3(NHC)$ complexes observes a correlation between these bond length and

ease of CO elimination. This leads to the definition of a new parameter r , repulsiveness. [Gusev, 2009b]

Repulsiveness is calculated as $r = 10 \cdot (7.568 - 0.003172TEP - 0.0446\Delta H)$. The repulsiveness is evaluated because it gives information about the stability of the catalytic complex. Higher repulsiveness means that the ligands tend to be more sterically demanding. This makes the catalyst more unstable, which can lead to easier elimination of other ligands. This can play a major role in catalysis if the elimination of a ligand, such as hydride, is desired. [Gusev, 2009b] This means that higher higher TEP values leads to a lower repulsiveness which makes catalysts more stable but therefore also less likely to eliminate ligands such as hydride.

The bond length of the metal to the main ligand is also a worthwhile parameter. [Gusev, 2009b] A relationship was found between the TEP, the bond length of the Ni-C and the Bond Dissociation Enthalpy. The relationship is defined as $\Delta H = 86.35 - 0.06741TEP + 21.63d(Ni - C)$. When comparing the investigated heterocyclic carbenes with phosphines, it is found that repulsiveness is higher in the carbenes and that they have higher bond lengths.

Bond dissociation enthalpies [Gusev, 2016] or ligand exchange enthalpies [Gusev, 2009a] are evaluated as a measure of the stability of the complex as a whole. The more difficult it is to remove a ligand, the higher the enthalpies involved. This is not always related to the catalytic activity, but it can be .

One of the oldest pieces of work on this topic is Tolman's investigation into electronic and steric parameters that give an indication of donor strength. [Tolman, 1977] This original work used $Ni(CO)_3L$ as a reference complex and has explored several tertiary phosphine ligands. It shows a trend between the A_1 stretching frequencies of the carbonyl groups and the coupling constant of the metal-phosphorous coupling found by NMR spectroscopy. Previous work had established that values of the coupling constant are correlated to the electronegativity of atoms attached to the phosphorous atom. This established the TEP as a measure of electron donor ability. [Grim, 1967] The TEP describes the net donating ability of the ligands in terms of the σ -donor ability and π -acceptor strength of the ligand, which can jointly be measured in the A_1 band in the IR spectrum. [Kühl, 2005]

1.2.2 Ruthenium

Any ligands used in a Ruthenium can be described by their TEP values. In previous work the TEP is never calculated or determined using ruthenium complexes. Instead a substitute rhodium complex with the same ligand is used to determine TEP values. [Grisi, 2016] Because the TEP can be evaluated with any metal this could be done by using whatever metals yields the easiest to synthesize complex or it could be done computationally. In his 2016 article Gusev does report carbonyl frequencies but he never establishes an official link to the TEP values, suggesting that a proper correlation between the frequencies of carbonyl in ruthenium and the TEP values of ligands has never been established. [Gusev, 2016]

The bond length between a central metal atom and the connecting ligand atoms is evaluated because it can be related to the stability of the catalyst. Gusev investigated Ruthenium YNP pincer complexes, which also had a Cl, H and CO ligand. [Gusev, 2016] The bond length of all the three connecting bonds between pincer ligand and metal atom was calculated, as well as the BDE of the Ru-Y bond. Although there is no direct correlation between any of these bond lengths and the found BDE. There was a link observed between the total size of the cyclical structure and the BDE, suggesting that a bigger ring leads to a more stable cyclical ligand, higher BDEs and therefore a more stable complex. Under standard conditions this might only be of limited relevance, but if the complex is to be used at higher temperatures, degeneration of the catalysts can be serious problem.

A study by Hwang c.s. established that hydricities in Ru complexes can be accurately determined by DFT, provided that proper corrections are included. [Nolan,

2009]. The hydricity of a complex is an important parameter because it shows the ease with which hydride ligands can be detached from the complex. In the catalytic reduction of carbonyl the formation of C-H bonds are always involved. The easier these can be made available from the catalytic complex, the higher the chance of a high catalytic activity. [DuBois, 2000]

1.2.3 Rhodium

Rhodium complexes are frequently used as an alternative for determining TEP values. The original Ni complexes are quite toxic and Rh complexes, such as $\text{RhCl}(\text{CO})_2\text{L}$ presents a safe and reliable alternative. [Chaplin, 2019] This same study also showed once again that a very strong correlation ($R^2 = 0.99$) exists between measured and calculated frequencies. TEP values for ligands in Rh complexes can be calculated using various correlation. One such is the correlation $\text{TEP} = 0.8001\nu_{\text{CO}}^{\text{Rh}} + 420.0$ which was found for $\text{RhCl}(\text{CO})_2(\text{NHC})$ complexes. [Glorius, 2010]

TEP is also evaluated because correlations between carbonyl stretching frequencies and the oxidation energy of the $\text{Rh}^{\text{I}}/\text{Rh}^{\text{III}}$ redox pair with various ligands within complexes. [Chaplin, 2019] This was done in $\text{Ir}(\text{PEP})\text{Cl}(\text{CO})\text{H}$ complexes, where PEP were diphenylphosphino-based pincer ligands. Related to this a modest negative correlation was found between the carbonyl frequencies and the chemical shift of the C atom found using ^{13}C NMR spectroscopy. [Chaplin, 2019]. This correlation is however largely reflective of the difference between the Rh^{I} and Rh^{III} variants, rather than then distinguishing between the various pincer ligands.

Bond dissociation energies were evaluated in NHC Rh complexes because it can be a measure of the steric hindrance of an NHC ligand. [Grisi, 2016] BDE are affected by electron donating abilities and the dimension of the substituents on the ligands. This first factors showed only minor differences, but the repulsive effects of large substituents was clearly visible.

A study by Hwang c.s. established that hydricities in Rh complexes can be accurately determined by DFT, provided that proper corrections are included. [Nolan, 2009] The hydricity of a complex is an important parameter because it shows the ease with which hydride ligands can be detached from the complex. In the catalytic reduction of carbonyl the formation of C-H bonds are always involved. The easier these can be made available from the catalytic complex, the higher the chance of a high catalytic activity. [DuBois, 2000]

1.2.4 Iridium

In the literature, different correlation can be found for deriving the TEP values of ligands within a iridium complex. Such a correlation makes it possible to compare ligands in an iridium complex with other ligands in the original Ni compounds used by Tolman. Originally the correlation ($\text{TEP} = 0.722\nu_{\text{CO}}^{\text{Ir}} + 593$) had been observed for $(\text{L})\text{Ir}(\text{CO})_2\text{Cl}$ complexes with phosphine ligands. [Crabtree, 2001] This correlation was later corrected to $\text{TEP} = 0.8475\nu_{\text{CO}}^{\text{Ir}} + 336.2$. These correlation were originally observed for phosphine ligands, and later extended to NHC ligands by Nolan. The TEP values show that NHC ligands have stronger donating abilities then the tertiary phosphine ligands and with lower variation between the various NHC ligands. [Nolan, 2008] Glorius, in his later work, assumes the correlation found by Nolan c.s. as this models his complexes. [Glorius, 2010].

The buried volume ($\%V_{\text{Bur}}$) in evaluated because Nolan found that the differences between various NHC ligands in the TEP value are vary minimal, while their catalytic activities vary quite extensively. He observed that there are significant steric effects in play and there is a need to quantify those. [Nolan, 2008]

Bond lengths and frequencies of C=C groups are of interest because not all complexes follow the structure of Tolman's original reference complex. Having three carbonyl groups and a hydride severely limits the options available for the defining ligand. Most transition metals will adopt a 6+ geometry so only a single ligand, with two connections to the central metal atom is applicable in this scenario. In time the field has expanded into other ligands, such as pincers. [Gusev, 2002] Often at least one carbonyl group is retained, to enable the three aforementioned properties to be calculated. But we see that the similarities with the original work is decreasing and with this come questions about the validity and applicability of the drawn conclusion.

The distance of this C=C bond and its stretching frequency show a similar relationship as the distance and frequency of a C=O bond in Ir complexes. When ranking donor properties of phosphines, C=C bonds show very similar patterns to C=O bonds and could be considered as a possible replacement, though values obviously differ. The study does note that the C=C bond appears to be more sensitive to steric effects. Bulky and medium sized ligands activate the C=C bond less than could be expected based on their electronic properties. This means that this parameter is primarily useful for smaller sized ligands. [Gusev, 2009a]

1.2.5 Manganese

Manganese complexes often include cyclopentadienyl ligands and the presence of this ligand affects the frequencies of any carbonyl groups used for determining TEP values. Kühl found a good correlation between the A_1 frequencies and the TEP of $TEP = 0.711\nu_{CO}^{Mn} + 692$ for $CpMn(CO)_2L$ complexes. This establishes the applicability of TEP values to some manganese complexes, but a correlation between the TEP and $Mn(CO)H_3L$ hasn't been published yet.

Quite some practical work has been done on manganese complexes with various ligands as catalysts. [Sortais, 2018], [Bruneau-Voisine, 2019] This work is mostly showing complexes with good catalytic activity but has not established links between this catalytic activity and other, computable, parameters.

Computational work thus far has mostly focused on catalytic pathways. DFT research shows us that the catalytic pathway of a carbonyl reduction in an ester involves the detachment of a hydride of the central metal (thus breaking a Mn-H bond) and of a proton from an adjacent group, like an amide, (thus breaking a N-H bond). [Pidko, 2018] The step wherein bonds are formed between the substrate and the complex is energetically very significant.

This means that the hydricity of the manganese complex and the acidity of the adjacent proton are very relevant factors in assessing the catalytic properties of a Mn complex.

Later work into the reduction of ketones showed involvement from the same hydrogen atoms and suggested investigating small bidentate ligands containing NHC groups as possible active and enantioselective Mn catalysts. [Pidko, 2019b]

2 | MATERIALS & METHOD

In this project various Manganese complexes with bidentate ligands have been investigated. All complexes fit the basic $\text{MnH}(\text{CO})_3\text{L}$ formula. The ligands chosen have all been subject to earlier work into their catalytic properties. Unfortunately these studies have been carried out under different circumstances, making it difficult to compare found catalytic activity or turn over number between all ligands. Only those ligands from the same study can be accurately compared when it comes to catalytic properties.

2.1 LIGANDS USED

The majority of the ligands investigated (34) is of the NN-type, where the ligand is connected to the Mn atom with two N atoms. Other types investigated are the CC(1), NC (3) and NP (6) type. The name of each complex is given by the two letter abbreviation of their type followed by a serial number. Some numbers are missing because the complexes involved proved to be defective during the work.

The following complex is based on work by Pidko. [Pidko, 2018]. It was used to evaluate the catalytic pathway of ester hydrogenation.

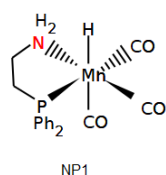


Figure 2.1: Ligands based on [Pidko, 2018]

The following complexes are based on another article by Pidko. The first four complexes are referenced in the article as having good reported activity, which led to Pidko and his coworkers to the formulation of the fifth complex (NC1), which was shown to be an highly active catalyst with a high turn over number and frequency even in low concentrations. [Pidko, 2019a]

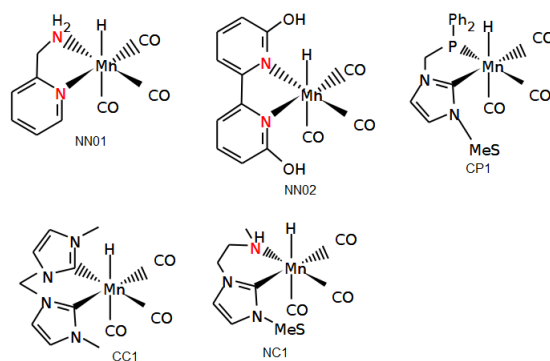


Figure 2.2: Ligands based on [Pidko, 2019a]

Here complexes based on work by Sortais and his coworkers are investigated. One of the complexes (NN01) is the complex that was cited by Pidko in his work. [Pidko, 2019a] In his study Sortais investigated the reduction of a wide range of ketones and aldehydes and found that the catalyst with both the hydrogen atoms at the N atom adjacent to the manganese (NN01) showed the highest catalytic activity. A single methyl substituent (NN04) slightly decreased this activity, while replacing both H atoms with methyl groups led to almost complete loss of catalytic activity. [Sortais, 2017]

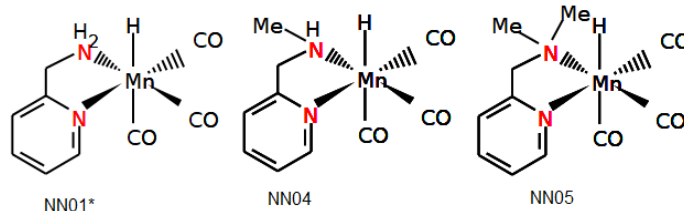


Figure 2.3: Ligands based on [Sortais, 2017]

In research that followed the previous mentioned article, Sortais and his coworkers expanded their work into nitrogen bidentate manganese catalysts. [Sortais, 2018] They evaluated a wide range of ligands of this type, which showed widely differing catalytic activities, ranging from a conversion ratio of 0% to 97% in the given environment. An interesting observation to make is that none of the ligands that did not have a hydrogen atom attached to the N atom adjacent to the manganese showed significant catalytic activity. This series also included three ligands from their previous project (NN01, NN04 and NN05). [Sortais, 2017].

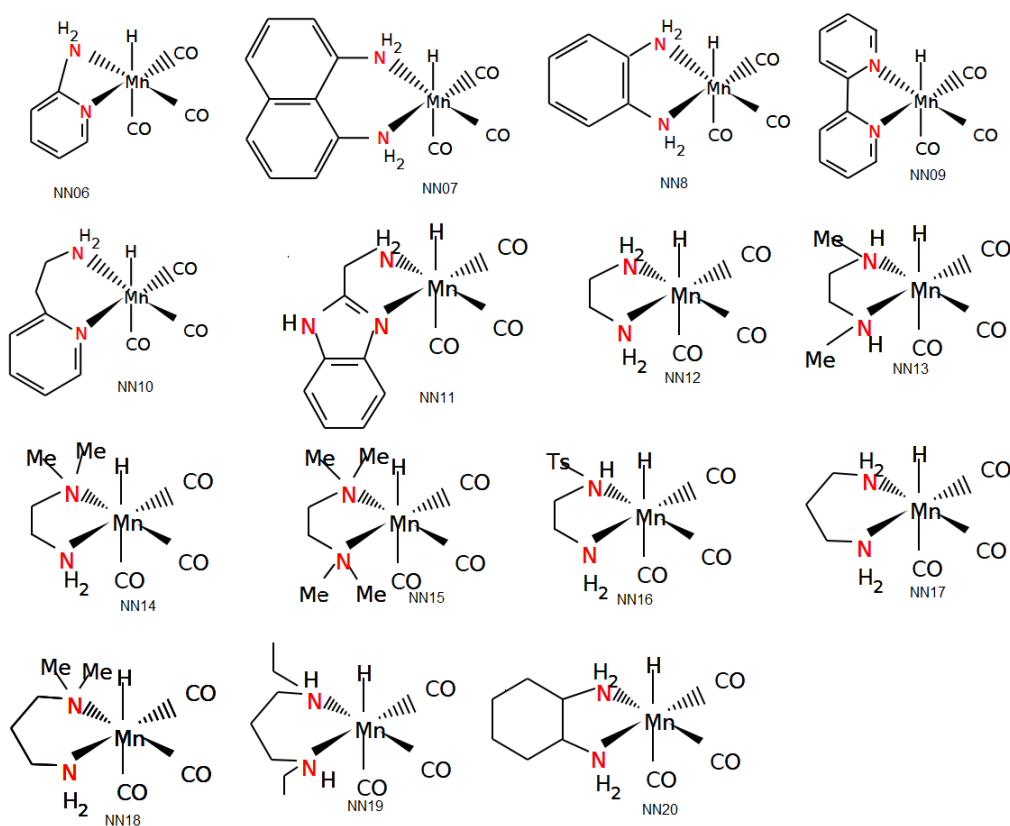


Figure 2.4: Ligands based on [Sortais, 2018]

Another study by Sortais and coworkers into the trans hydrogenation of aldimines used two other bidentate manganese catalysts. [Sortais, 2019]

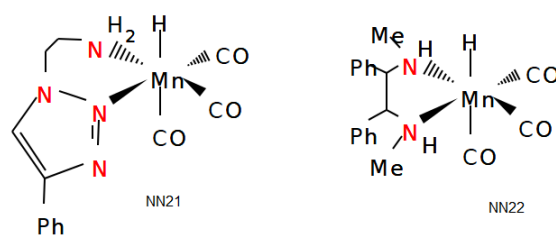


Figure 2.5: Ligands based on [Sortais, 2019]

Transfer hydrogenation has been studied wider. Pidko c.s. used in-situ manganese NN and NP catalysts for asymmetric transfer hydrogenation of acetophenone. Notable in this study was that the NP catalysts (NP2, NP3 and NP4) showed higher conversion rate (91%, 90% and 91%) than the NN bidentates. The enantiomeric excess was, however, quite low (8%, 2% and 20% respectively) for these complexes. Compared with this some the NN complexes generated much higher ee values, up to 69% and 76 %. [Pidko, 2019b]

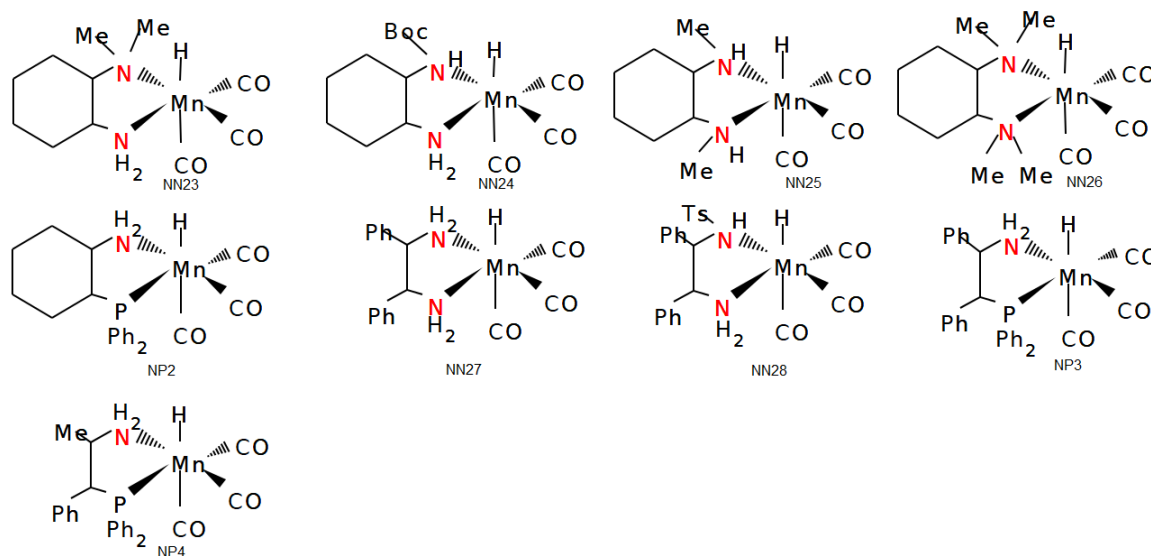


Figure 2.6: Ligands based on [Pidko, 2019b]

A computational study into the mechanisms of ligands in catalysing the hydrogenation of CO₂ was done by Pathak c.s. [Pathak, 2019] Their work included eighth different complexes, including two complexes we encountered previously in the work of Sortais (NN01, NN04).

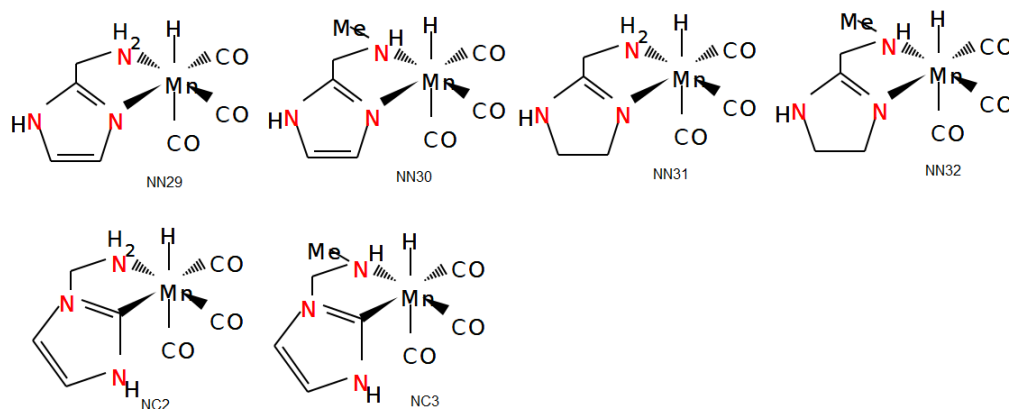


Figure 2.7: Ligands based on [Pathak, 2019]

Aminotriazole Mn(I) complexes have been found to be effective catalysts (yields of 81% to 87%) for the hydrogenation of ketones by Leitner and his coworkers. [Leitner, 2018]

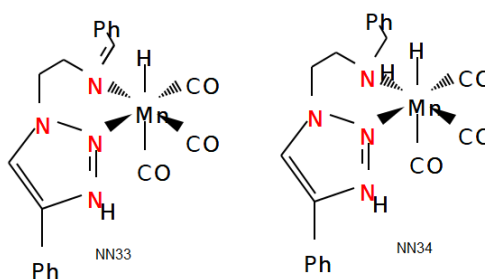


Figure 2.8: Ligands based on [Leitner, 2018]

2.2 MODELS MADE

For each ligand several models were made using GaussView.

- The base ligand
- The base complex $\text{MnH}(\text{CO})_3\text{L}$
- The three derivatives of the base complex with 1,2 or 3 carbonyl groups removed
- The base and derivate complexes without the hydride ligand
- If applicable: the base and derivate complexes with both the hydride ligand and a proton from an adjacent atom removed.

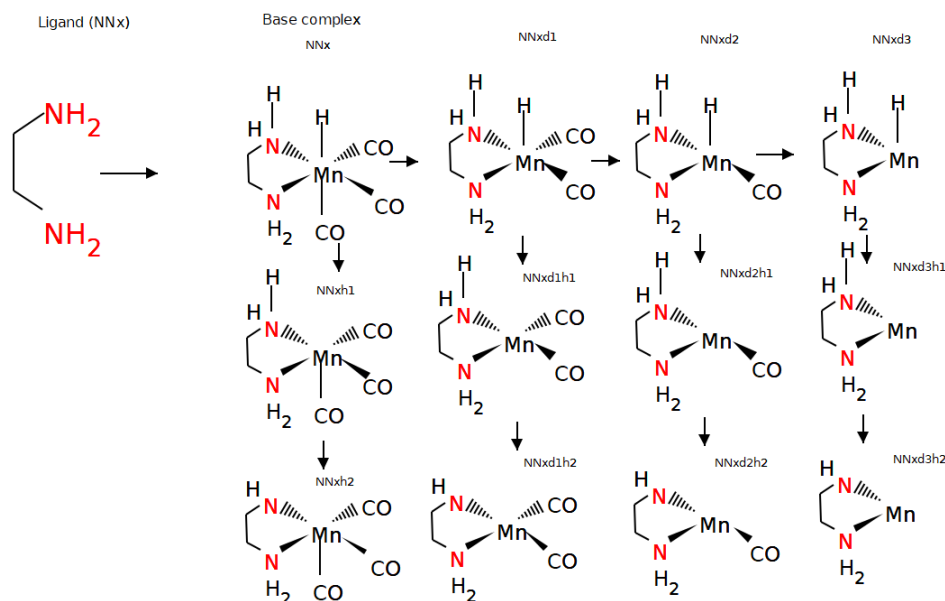


Figure 2.9: All models per ligand

This yields a total of either 9 or 13 models per ligand depending on the presence of a H atom adjacent to the central Mn atom.

2.3 PARAMETERS EVALUATED

All density functional theory (DFT) calculations were performed using the Gaussian16 Co.1 program.⁵⁴ The hybrid exchange-correlation functional PBE0⁵⁵ was used in combination with the 6-311+G(d,p) basis set on all atoms for geometry optimization and vibrational analysis. Van der Waals interactions are accounted for by the dispersion-corrected DFT-D3 (BJ) method.⁵⁶ The ultrafine grid was uniformly used.

Based on the results of these calculations the following parameters were evaluated:

- The hydricity of the complex (in kcal/mol)
- The acidity of the H atom adjacent to the hydride if applicable (in kcal/mol)
- The A_1 stretching frequencies of the base complex (in cm^{-1})
- The length of the CO bond (in Å)
- The bond lengths of the Mn and connecting atoms in the ligand (in Å)
- The Bond Dissociation Energy of the ligand (in kcal/mol)
- The decarbonylation enthalpy of the first, second and third carbonyl group (in kcal/mol)

2.4 MOLSIMPLIFY

Attempts were made to include the software molSimplify into this project. MolSimplify is a packaged developed at the Kulik research group at the Massachusetts Institute of Technology. [Kulik, 2016] It is open source python code that can generate geometries of transition metal complexes for use as input in DFT calculations.

MolSimplify can be accessed via the commandline and input can either be given via this commandline or by using input files. When using a UNIX system, there is also a Graphical User Interface (GUI) available that can be used to access some functionality. This GUI is not necessary and its function is to compile an input file using the details entered by the user. This input file is then immediately processed by the code, but also exported separately for review purposes.

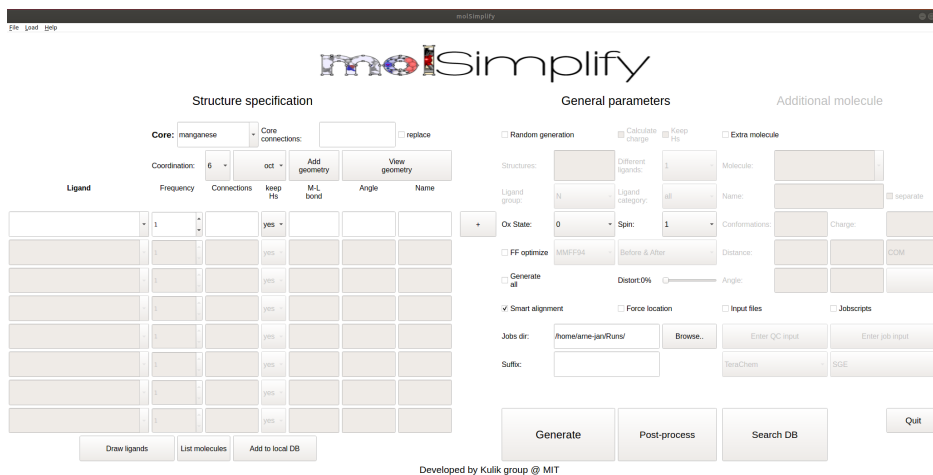


Figure 2.10: The molSimplify GUI

The main purpose of the software is generating input files but it claims several advantages over generating input files using GaussView, Avogadro or similar modelling software. It offers possibilities to generate not just one but a whole range of structures by automatically making modification to one or more ligands. This means that only one model of the ligand has to be modelled in advanced and that a range of simple modifications such as adding methyl or fenyl groups can be done automatically.

Apart from this automation the software also claims to be able to predict the outcome or success of DFT calculations. [Kulik, 2019] These predictions can prevent

DFT calculation attempts on structures that will not yield a stable structure and therefore lead to failure and wasted time and resources.

When installing the package, it automatically downloads a ligand database. All functionalities of this database and all the basic calculations can be used without internet access using just your local processor capacity. There is the option to extend to included database with existing chemical databanks such as the ChEMBL database, which is a large open-source database of bio-active molecules maintained by the European Bioinformatics Institute. To do this you need to download the databank in .sdf and extract it to the correct place in the molSimplify file-path.

MolSimplify can then be given a series of search criteria, such as having a certain type of atom available for coordination (such as N or P), excluding compounds with certain atoms or setting upper or lower limits of the overall size of the molecule. With these criteria the query will generate a file with SMILES strings for all entries that meet that search criteria. Further queries can be done on the results of the first query which can further narrow down the amount of possible options.

MolSimplify has quite a big database of common ligands, such as ammonia, CO, amino acids, pyridine and many others. When a ligand that is not available in the database is desired, it can be included in several ways. First option is to provide a separate .xyz file which contains a model of the desired ligands. This is the route that we took, and .xyz files of all ligands were prepared using Avogadro. Alternatively it is possible to enter a SMILES string, eliminating the need for separate files. When certain ligands are used frequently it is also possible to add them to the local database for easy access. One shortcoming of the package is the absence of a hydride ligand in the database, but this is easily solved.

Unfortunately molSimplify was unable to generate the desired bidentate complexes. The reasons for this failure is not completely understood. The results that we did get however, suggest that the problem lies in the ligand models that were used.

When making a complex in molSimplify, you start by selecting the core. In our cases this was the single atom Mn, but the program is equipped to deal with more complicated centres as well. It is possible to select all sorts of metal atoms, salt fragments or even a complete complex as a base. Examples of this are a range of porphyrin complexes, ferrous oxide (specifically Fe_2O_2) or $\text{Fe}(\text{N}_4\text{Py})$.

Following the selection of the core atom(s), we can select the coordination number and geometry of the complex. Coordination numbers vary from 1 to 8 and come with accompanying geometries. It is possible to add additional geometries to the database and it is possible to visualise the geometry chosen using the 'view geometry' button.

After defining the core we have to select the desired ligands. This can be done by choosing a ligand from the databank using the dropdown menu in the GUI. Alternatively the filepath to an .xyz or a SMILES string can be entered in the same field. Below are the ligands used to generate complex NNo1. Next we define the frequency of the ligand within this complex, whether the ligand keeps all H atoms on the coordinating atom (the default is that this will happen) and, if required, we can fix the bond length and angle and label the bond.

If we use the settings shown in Figure 2.11 and generate the structure we get the following result.

This is not the structure of the complex we want. This is because of two reasons; the wrong atom is used as the coordinating atom and there is only one connection between the ligand and the core and not the two connections the bidentate requires.

We can define which of the atoms of the ligand will serve as the coordinating atom. This can be done by evaluating the ligand by pressing the 'draw ligands' button. This causes a popup window with 2D modules of the ligands to appear. In this model all atoms in the ligands will be numbered.

By default, atom number 1 will be used as the coordinating atom, as we can see in Figure 2.12. If another atom needs to be used, the number of that atom can be

| Ligand | Frequency | Connections | keep Hs | M-L bond | Angle | Name |
|------------------------|-----------|-------------|------------|-------------|-------|------|
| co | 3 | | no | | | |
| ~/Avogadro/H.xyz | 1 | | yes | | | |
| ~/Avogadro/ligNN01.xyz | 1 | | no | | | |

Figure 2.11: Entering the desired ligands in the GUI

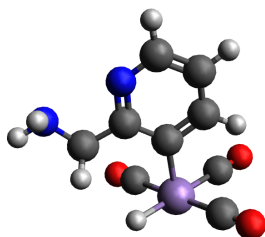


Figure 2.12: The structure generated

entered in the 'Connections' field of the ligand. If we want two connections we can enter two numbers in the 'Connections' field. So to generate the structure of complex NN01 we need to enter the following information.

Unfortunately using this set of specifications does not yield a usable complex, but causes molSimplify to crash and the GUI to close. When we simplify the instructions to only include a single bond between the ligand and the core, so only enter '9' or '12' instead of '9, 12' the same crash happens.

One possible cause could be that the used ligand is somehow too complex. When we use a simple ligand, such as ligand NN12, (ethylenediamine) the structure generates when we use the default atom 1 but the software crashes when we specify the N atoms as the coordinating atoms. Ethylenediamine is, however, one of the ligands that is predefined in molSimplify's database. When we use the database entry for ethylenediamine, instead of the .xyz file, the bidentate complex is generated correctly even without any coordination specifications.

This means there is a difference between the database entry for ethylenediamine and our own model. When we compare the 2D models of the database model and our own .xyz file, we see no difference, except for the numbering.



Figure 2.13: The 'Draw ligands' popup window

Structure specification

Core: Core connections: ☐ replace

Coordination:

| Ligand | Frequency | Connections | keep Hs | M-L bond | Angle | Name |
|---|--------------------------------|------------------------------------|----------------------------------|----------------------|----------------------|----------------------|
| <input type="text" value="co"/> | <input type="text" value="3"/> | <input type="text"/> | <input type="text" value="no"/> | <input type="text"/> | <input type="text"/> | <input type="text"/> |
| <input type="text" value="~/Avogadro/H.xyz"/> | <input type="text" value="1"/> | <input type="text"/> | <input type="text" value="yes"/> | <input type="text"/> | <input type="text"/> | <input type="text"/> |
| <input type="text" value="~/Avogadro/ligNN01.xyz"/> | <input type="text" value="1"/> | <input type="text" value="9, 12"/> | <input type="text" value="yes"/> | <input type="text"/> | <input type="text"/> | <input type="text"/> |

Figure 2.14: Generating complex NN01

Evidently manually selecting the right atoms is not enough to get the same result with our own model. There is the options to add new ligands to molSimplify's database. When selecting this options, a .xyz file or SMILES string needs to be entered and several other pieces of information needs to be provided. Somewhere either in the file or in this additional information must be the difference between molSimplify crashing and successfully generating a structure: but unfortunately we have not been able to find out what causes this difference and therefore were not able to generate any complexes that use non pre-defined ligands.

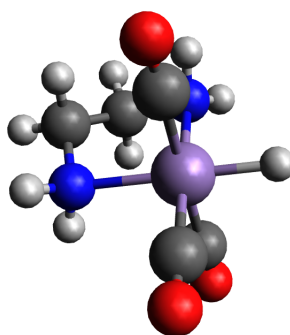


Figure 2.15: Complex NN12 generated by molSimplify

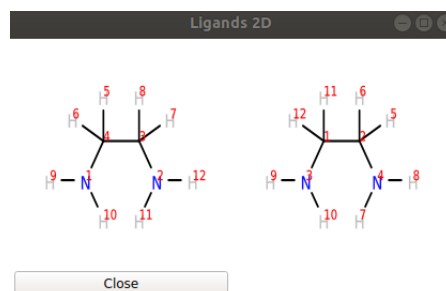


Figure 2.16: Ethylenediamine, the database version on the left

Insert/remove to/from Database

Database Update

Select type:

SMILES or file:

Name:

Groups:

Category:

☒ FF before ☒ FF after

Denticity:

Catoms:

Figure 2.17: Window for inserting ligands to the database

3

RESULTS & DISCUSSION

A complete overview of the numerical results can be found in the Supporting Information. For the broadest plots a total of 39 evaluated complexes were used.

Sometimes certain derivatives did not yield stable structures during multiple calculation attempts. This is the reason why some fields within the tables are in the supporting information are empty and why not all plots have the same number of data points.

3.1 THE CO LIGANDS

The analysis of the base complexes yields multiple frequencies around the 1950 - 2150 cm^{-1} region, involving the CO groups. We consistently find that the highest of these frequencies is the A_1 stretching frequency, which is used by the TEP. [Tolman, 1977] Because no exact correlation is known to correlate A_1 stretching frequencies in these particular kind of complexes to the TEP we will not report the values as TEP values, but refer to that as the A_1 CO frequency.

There are no known TEP value for any of our ligands, so unfortunately it is not possible to derive a TEP expression for this type of complexes.

Gusev showed a correlation exists between the stretching frequency and the CO bond length. [Gusev, 2009a] When we plot our found A_1 stretching frequencies and the average CO bond length we find the scatter plot below. For this plot we used data from a total of 39 evaluated complexes.

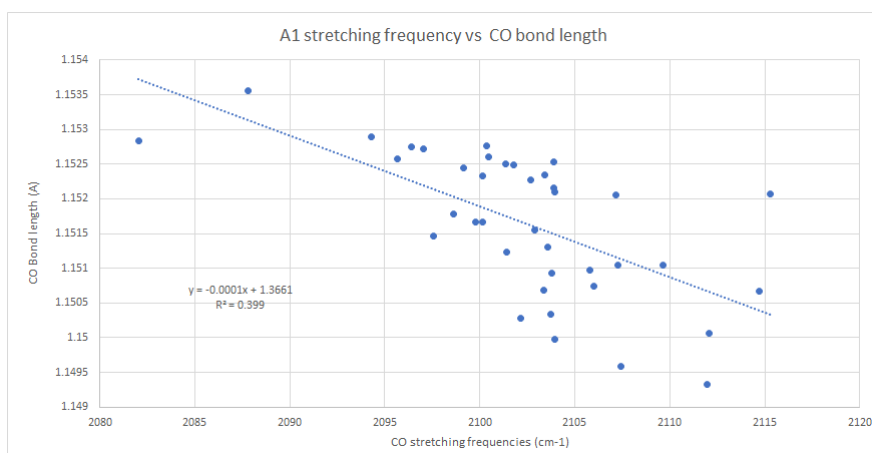


Figure 3.1: A_1 frequency vs CO bond length

We observe that this does not yield a good correlation. With an R^2 value of 0.399, we must conclude that we do not observe a proper correlation between the A_1 CO stretching frequency and the CO bond length.

In another paper Gusev shows a connection between the TEP, or A_1 frequency, and the decarbonylation enthalpy of the first CO-group, and the distance between the metal atom and the ligand. [Gusev, 2009b] We can observe that all the decarbonylation enthalpies show an increasing trend from the first, to the second, to the third carbonyl group. If we plot the decarbonylation enthalpy vs the A_1 frequency and the CO bond length we find the follow plots.

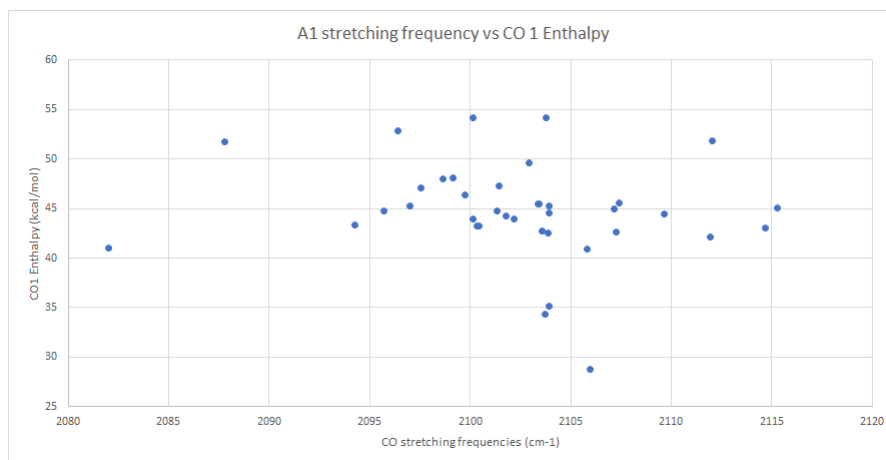


Figure 3.2: A_1 frequency vs CO1 enthalpy

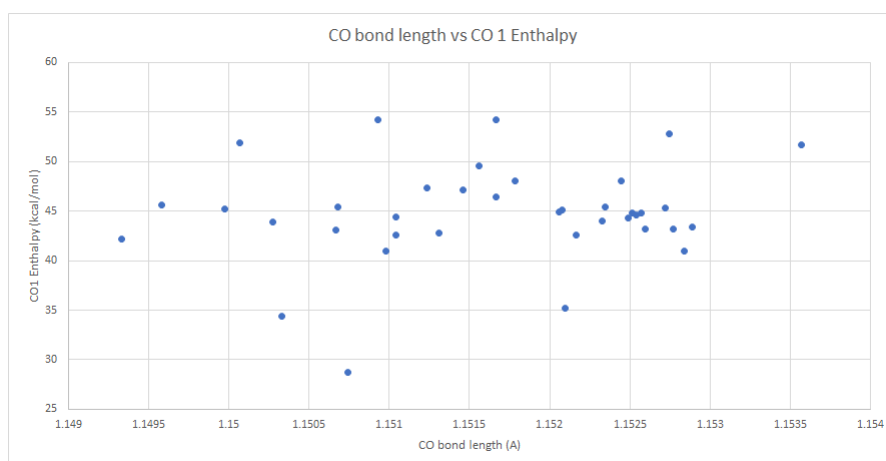


Figure 3.3: CO bond length vs CO1 enthalpy

We see that there is no correlation whatsoever between these parameters.

3.2 OTHER PARAMETERS

It is also interesting to look at the distance between the distance between metal and ligand. We have two bond lengths to characterise this. In some papers it has been suggested that it is not the individual bond length, but the overall length of the cyclical structure. [Gusev, 2016] In that regard it is interesting to plot the sum of these two bond length vs the BDE of the ligand.

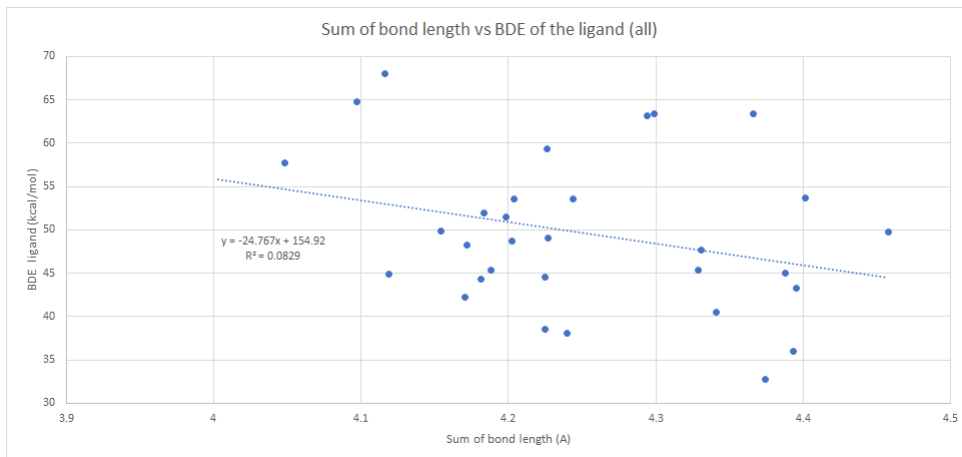


Figure 3.4: Sum bond length vs BDE ligand (All)

We observe there is no correlation here.

It would make sense to expect correlations within certain groups of ligands. It may therefore improve the correlation if we just examine one category of ligands at a time, such as only looking at the ligands with two nitrogen atoms bonded to the central metal. The NN-group is the only group big enough to justify plotting it on its own, the other groups contain too few data points to give meaningful information.

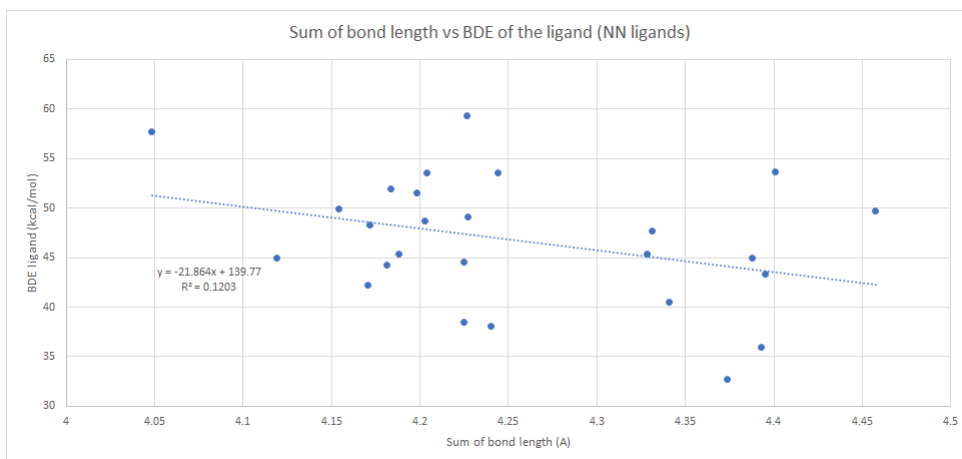


Figure 3.5: Sum bond length vs BDE ligand (NN)

We observe a slight improvement in the trend line, but there is no proper correlation to be observed.

A lot of mention is given to the values of both the TEP (or in our case A_1 stretching frequency), the hydricity and the acidity in various literature about catalytic activity. It is interesting to see if we can observe a correlation between the A_1 frequency and the hydricity/ acidity. This yields the plots below. All 39 compounds were used for the hydricity plot. A total of 29 data points is included in the acidity plot because not all compounds have secondary hydrogen atoms.

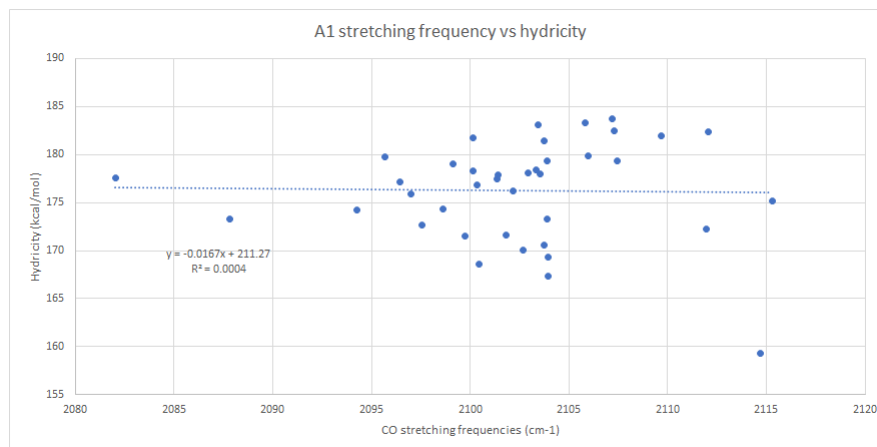


Figure 3.6: A1 frequency vs hydricity

We observe no correlation between the hydricity and the CO frequency. We can notice few main out-liners in this data-set those are complexes NN18 and CC1 on the left side and NN21, N33 and N34 on the bottom right side.

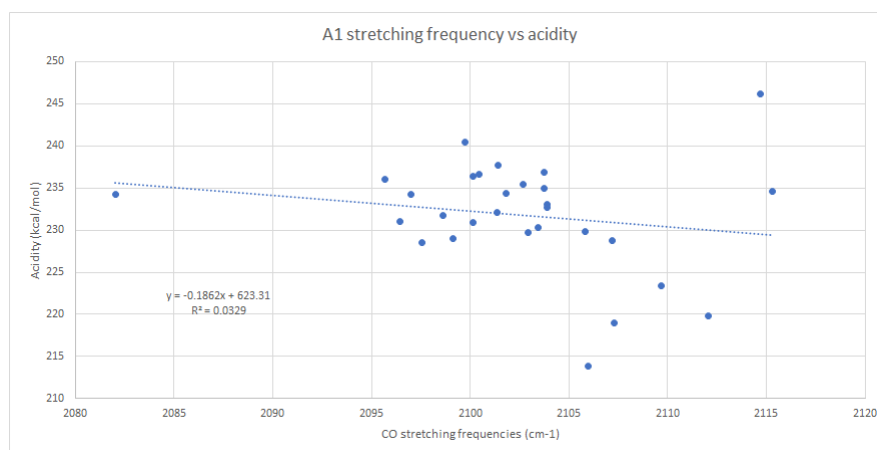


Figure 3.7: A1 frequency vs acidity

We observe no correlation between the acidity and the CO frequency. We can notice three main out-liners in this data-set those are complexes NN18 on the left and NN21 and NN34 in the top right side.

When we compare these out-liners and take into account that CC1 and NN33 do not appear in the acidity plot due to it not having a secondary hydrogen, we notice that the out-liners are the same complexes in both data-sets.

NN18, CC1, NN21 and NN34 are noticeable in the hydricity plot because they have the lowest and highest values for their CO frequency. NN34 represent both a high CO frequency and a very low hydricity, which makes it much more noticeable than other outliers. NN21 and NN31 have high CO frequency as well, but a hydricity much more within the mainstream (175 and 170 kcal/mol). However these three data points together, NN21, NN33 and NN34 together represent an oddity in the plot. These three point represent the only data points which have a high CO frequency but a comparatively lower hydricity. Without these three points we could say that there appears to be an effect where higher CO frequencies (> 2105) seems to lead to higher (> 175) hydricity values.

When we look at the acidity, we see a similar effect. Again NN18 represents the lowest CO frequency and we observe a similar effect with NN21 and NN34 as we saw in the hydricity plot, except this time it is reversed. NN33 is absent in this plot because it does not have a secondary hydrogen atom.

Again NN21 and NN 34 represent high CO frequency and this time much higher acidity then the other compounds. NN34 is again the biggest out-liner, with the highest value in the entire set (246). Here again there appears to be a trend. Compounds with higher frequencies (> 2105) appear to show lower acidity (< 230). This is the reverse of what was observed in the hydricity plot.

When we compare the complexes that yielded this effect we notice that NN21, NN31 and NN34 do represent three similar ligands.

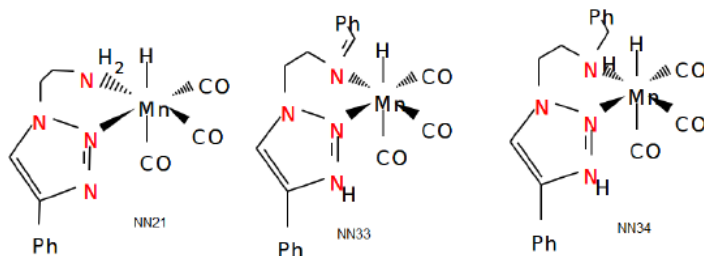


Figure 3.8: Ligands 21, 33 and 34

Because of this similarity it is not probable that these out-liners are errors, since similar ligands yield similar results. The total amount of complexes of this kind of structure is limited so it is difficult to draw any hard conclusion but it appears that including a ligand of this shape yields much lower hydricity and much higher acidity when compared to other ligands of similar CO frequencies.

3.3 COMPARISON WITH KNOWN CATALYTIC ACTIVITY

Most of the complexes evaluated came from studies which described their catalytic properties. This means that apart from our own calculated data we can rely on the data collected in those initial studies. We can use this to draw several conclusion.

Complexes without an H^+ energy value, so with no adjacent hydrogen atom to the hydride ligand, all have bad catalytic activity with regards to the reduction of carbonyl groups. This conclusion is not novel and is supported by the findings of previous experimental work [Sortais, 2018] and by our knowledge about the catalytic pathways [Pidko, 2018]. It is worth stressing again that any complex to be used for the catalytic reduction of carbonyl groups should have an amine group, or other proton donor, in the ligand adjacent to the Mn atom.

This also leads us to conclude that the TEP, or in our case the stretching frequency of the carbonyl groups is only of limited use to us. This parameter might give information about the electron donating properties of the ligand used, but this is not the determining factor for successful catalysis. Without the second H atom, the electron donating properties are almost irrelevant.

We can take a more in-depth look at a group of ligands from the same source: the work of Sortais. [Sortais, 2018]. These ligands (NN01 and NN04 to NN20 in our research) have reported conversion rates in the original article.

All these conversion rates were gathered under similar circumstances as described by Sortais. It represents the reduction of acetophenone in the presence of $Mn(CO)_5Br$ (0.5mol%), the ligand (0.5 mol%) and $tBuOK$ (1 mol%) in 2-propanol under 80 C for 1h. The conversation was determined by H NMR. [Sortais, 2018]

We can try to correlate this conversion rate to the the A_1 frequencies, the hydricity and the acidity of the ligand. This yields the plots on the following page.

We can observe no correlation between the conversion rate and these three parameters.

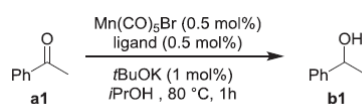


Figure 3.9: Scheme by Sortais

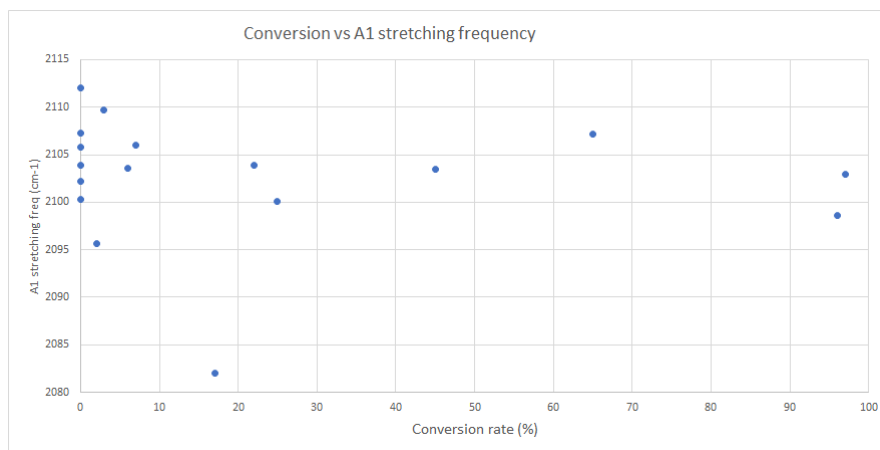


Figure 3.10: Conversion rate vs A1 frequency

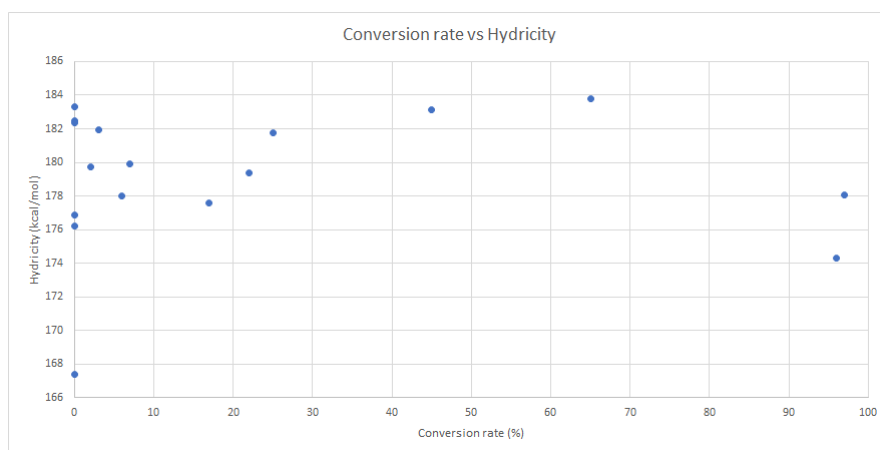


Figure 3.11: Conversion rate vs hydricity

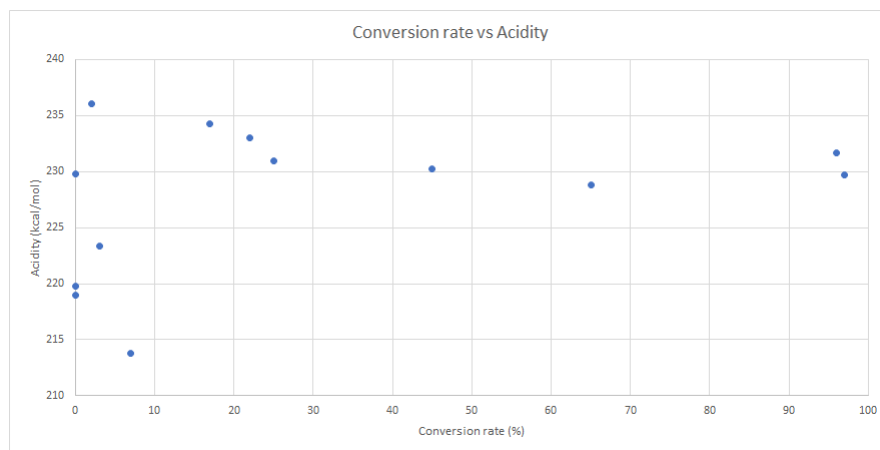


Figure 3.12: Conversion rate vs acidity

4 | FUTURE WORK

Based on the results and the literature we can make some recommendations for future research.

4.1 FINDING A CORRELATION FOR THE TEP IN MANGANESE BIDENTATE COMPLEXES

It has been established that TEP values for ligands can be found from other metals than Ni by using correlations. It has also been found that it is generally acceptable to calculate the required A_1 frequencies instead of measuring them experimentally. Though it would be preferable to have some experimental measurements to calibrate the degree of error in the calculation.

The bidentate complexes we used have two problems. First of all, no known TEP values exist for the bidentate ligands we used. On the other hand no TEP correlation exists for the type of complex $(\text{MnH}(\text{CO})_3\text{L})$ that we used. Because both of these pieces of information are missing, no conclusion about TEP values could be drawn. Future work could establish this. Ideally some of the ligands used in experimental work by Pidko or Sortais are used to generate Ir complexes, which can then be used to measure the A_1 stretching frequency and calculate the TEP. Once a TEP value is known, the frequencies in this work can be correlated to those values and an expression for TEP values in $(\text{MnH}(\text{CO})_3\text{L})$ complexes can be established.

4.2 ALTERNATIVES FOR THE TEP

We have seen that the TEP or its associated A_1 frequency is only of limited value in predicting catalytic activity. While it may still have its use as a measure of overall ligand donor strength, this one parameter is not decisive enough to base predictions on.

Another problem with the TEP is that the carbonyl groups are not truly independent observers. There is interference from various sources present which contaminates the TEP value. [Cremer, 2016]

Criticism of the TEP has been raised before and there has been some work on an alternative more sophisticated method. In a 2016 study, Cremer and his coworkers proposed an alternative parameter, the Metal-ligand electronic parameter (MLEP). [Cremer, 2016] This parameter is based on the metal ligand stretching force constant of an individual bond and is therefore a localised value, instead of an overall average. The MLEP also contains within itself any destabilizing steric interactions between the metal and the ligand, which the TEP cannot account for and which prompts the need for a second parameter.

Their original work focused on Ni and 181 different types of ligands and this was later expanded to other transition metal such as Au, Ru, Rh and Ir. [Cremer, 2017] An expansion into Mn would be a logical step and could prove of value in the work with manganese catalysts that is being done here.

4.3 MOLSIMPLIFY

The molSimplify code has promising features but many of the ligands used in this project were not included into the database that comes with the base package. We have found that our own models, in the form of .xyz files of the ligands, did not yield the required results. The software does not appear to be fundamentally flawed, since that ligands that are present in the database do generate the desired complexes. More work is needed to evaluate what aspects of the models are flawed and how they can be improved for our required purpose.

The results of the DFT calculations with regards to the CO ligands are shown in the table below.

| name | CO freq (A1) (cm-1) | av. CO length (Å) | CO 1 Enthalpy (kcal/mol) | CO2 Enthalpy (kcal/mol) | CO 3 Enthalpy (kcal/mol) |
|-------|------------------------|----------------------|-----------------------------|----------------------------|-----------------------------|
| NN1 | 2102.9116 | 1.151557 | 49.57281 | 52.44687 | 52.69131 |
| NN2* | 2103.9337 | 1.149976667 | 45.22959 | 47.00619 | 45.71343 |
| NN4 | 2098.6228 | 1.151784667 | 48.01671 | 48.81051 | 55.78209 |
| NN5* | 2103.5526 | 1.151307333 | 42.78015 | 52.88157 | 57.05595 |
| NN6 | 2112.0696 | 1.150067 | 51.87861 | 48.84201 | 54.88434 |
| NN7 | 2109.6632 | 1.151041333 | 44.4402 | 56.34468 | 60.49134 |
| NN8 | 2107.2877 | 1.151044333 | 42.59745 | 55.93266 | 61.17363 |
| NN9* | 2102.1646 | 1.150272667 | 43.9362 | 50.25258 | 50.02137 |
| NN10 | 2105.9771 | 1.150739667 | 28.74627 | 64.6947 | 49.81095 |
| NN12 | 2107.169 | 1.152055667 | 44.94168 | 57.56688 | 62.21943 |
| NN13 | 2103.4282 | 1.152342667 | 45.45702 | 57.27078 | 64.4301 |
| NN15* | 2100.3352 | 1.152767 | 43.22997 | 56.9835 | 59.11605 |
| NN16 | 2105.7955 | 1.150976333 | 40.95252 | | |
| NN17 | 2100.13 | 1.152324 | 43.99542 | 53.7327 | 61.67637 |
| NN18 | 2082.026 | 1.152838667 | 40.98024 | 54.17181 | 62.65035 |
| NN19 | 2095.6808 | 1.152572333 | 44.80812 | 51.96492 | 62.76753 |
| NN20 | 2103.9043 | 1.152540333 | 44.59896 | 57.92724 | 62.38512 |
| NN21 | 2115.2868 | 1.152074333 | 45.08658 | 53.22996 | 54.05211 |
| NN22 | 2101.3575 | 1.152511333 | 44.76591 | 57.42513 | 60.74271 |
| NN25 | 2097.0145 | 1.152718333 | 45.31842 | 57.43332 | 61.8408 |
| NN26* | 2094.2728 | 1.152888667 | 43.39125 | 56.93247 | 63.25641 |
| NN27* | 2103.9302 | 1.152095 | 35.18487 | 64.74321 | 62.82738 |
| NN28 | 2103.7252 | 1.150333333 | 34.39107 | 52.60626 | 39.57786 |
| NN29 | 2103.893 | 1.152164 | 42.57414 | 56.26908 | 61.88175 |
| NN30 | 2101.7963 | 1.152492 | 44.27136 | 56.17458 | 60.77484 |
| NN31 | 2102.6708 | 1.152267333 | | | |
| NN32 | 2100.4622 | 1.152598333 | 43.24005 | 56.49336 | 60.13224 |
| NN33* | 2111.9568 | 1.149333333 | 42.15393 | 48.22587 | 48.61647 |
| NN34 | 2114.7017 | 1.150666667 | 43.09389 | | |
| NP1 | 2103.7621 | 1.150929 | 54.20709 | 48.69963 | 59.94009 |
| NP2 | 2101.4251 | 1.151237333 | 47.33694 | 56.89278 | 58.14018 |
| NP3* | 2099.7539 | 1.151666667 | 46.39068 | | |
| NP4 | 2100.1484 | 1.151666667 | 54.20205 | 50.6646 | 54.96309 |
| NP5* | 2103.3587 | 1.150678333 | 45.47214 | 51.18183 | 59.47641 |
| NP6 | 2107.4254 | 1.14958 | 45.57672 | 50.49576 | 58.4514 |
| CC1 | 2087.8048 | 1.153565667 | 51.70977 | 51.56298 | 51.07662 |
| NC1 | 2097.5574 | 1.151462667 | 47.11203 | 47.03328 | 56.39508 |
| NC2 | 2099.1406 | 1.152446333 | 48.05766 | 50.77548 | 62.26605 |
| NC3 | 2096.4235 | 1.152747667 | 52.82487 | 50.11965 | 58.71537 |

Table 5.1: Results CO ligand

The rest of the parameters are measurements about the functional ligand. These results are shown in the table below.

| name | hydricity (kcal/mol) | H+ energy (kcal/mol) | Bond Mn-L (Å) | Bond Mn-L (Å) | BDE ligand (kcal/mol) | Conversion |
|-------|-------------------------|-------------------------|------------------|------------------|--------------------------|------------|
| NN1 | 178.07076 | 229.71312 | 2.054291 | 2.099929 | 49.9275 | 97 |
| NN2* | 167.38785 | | 2.051185 | 2.051188 | | |
| NN4 | 174.31596 | 231.7203 | 2.116101 | 2.244225 | | 96 |
| NN5* | 178.01973 | | 2.041079 | 2.157267 | 51.49809 | 6 |
| NN6 | 182.38248 | 219.7692 | 2.02486 | 2.15655 | 44.28396 | 0 |
| NN7 | 181.92132 | 223.3602 | 2.119969 | 2.119886 | 38.04507 | 3 |
| NN8 | 182.50281 | 218.93949 | 2.170348 | 2.170733 | 40.53735 | 0 |
| NN9* | 176.19147 | | 2.024206 | 2.02418 | 57.72816 | 0 |
| NN10 | 179.91036 | 213.82578 | 2.183032 | 2.190831 | 32.72724 | 7 |
| NN12 | 183.78045 | 228.77757 | 2.11329 | 2.113718 | 49.1022 | 65 |
| NN13 | 183.13533 | 230.25555 | 2.121396 | 2.122561 | 53.56134 | 45 |
| NN15* | 176.88447 | | 2.164672 | 2.166291 | 47.67651 | 0 |
| NN16 | 183.30669 | 229.80069 | 2.141107 | 2.232928 | | 0 |
| NN17 | 181.78839 | 230.92839 | 2.155578 | 2.172824 | 45.41166 | 25 |
| NN18 | 177.6159 | 234.29007 | 2.161393 | 2.233792 | 43.32699 | 17 |
| NN19 | 179.73963 | 236.02761 | 2.180129 | 2.207642 | 44.97003 | 2 |
| NN20 | 179.39754 | 233.02944 | 2.101158 | 2.102456 | 53.52291 | 22 |
| NN21 | 175.22001 | 234.55026 | 2.037209 | 2.133441 | 42.18354 | |
| NN22 | 177.48423 | 232.10775 | 2.110847 | 2.115434 | 59.35734 | |
| NN25 | 175.87521 | 234.30708 | 2.189092 | 2.21197 | 53.64702 | |
| NN26* | 174.22776 | | 2.227871 | 2.229729 | 49.75425 | |
| NN27* | 169.28856 | | 2.100558 | 2.124403 | 44.50635 | |
| NN28 | 170.57061 | 236.86299 | 2.163 | 2.23 | 35.97615 | |
| NN29 | 173.313 | 232.74657 | 2.051574 | 2.13673 | 45.36378 | |
| NN30 | 171.62334 | 234.37701 | 2.046209 | 2.15648 | 48.70467 | |
| NN31 | 170.02566 | 235.46691 | 2.034938 | 2.136696 | 48.28761 | |
| NN32 | 168.5691 | 236.67525 | 2.029882 | 2.153807 | 51.98256 | |
| NN33* | 172.23948 | | 2.025 | 2.094 | 44.91963 | |
| NN34 | 159.27786 | 246.21597 | 2.17 | 2.055 | 38.51316 | |
| NP1 | 181.43748 | 234.93204 | 2.13128 | 2.256392 | | |
| NP2 | 177.91767 | 237.76578 | 2.119005 | 2.247162 | 63.36225 | |
| NP3* | 171.55089 | 240.45966 | 2.14 | 2.244 | | |
| NP4 | 178.35489 | 236.43081 | 2.136 | 2.252 | | |
| NP5* | 178.44939 | | 2.092541 | 2.206573 | 63.4221 | |
| NP6 | 179.38998 | | 2.093323 | 2.200622 | 63.19404 | |
| CC1 | 173.2941 | | 2.001373 | 2.001663 | | |
| NC1 | 172.68741 | 228.58101 | 2.028232 | 2.291516 | | |
| NC2 | 179.04537 | 229.00815 | 1.95424 | 2.142703 | 64.76085 | |
| NC3 | 177.19821 | 231.05817 | 1.952679 | 2.16373 | 68.01795 | |

Table 5.2: Results functional ligand

Ligands marked with an asterisk do not have an H-atom on the coordinating atom and do therefor not have an acidity.

Sometime certain derivates did not yield stable structures during multiple calculation attempts. This is the reason why some fields within the tables are empty.

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